

DETERMINATION OF THE CHARGE OF POSITIVE THERMOINS FROM
MEASUREMENTS OF THE SHOT EFFECT

A DISSERTATION
SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE
UNIVERSITY OF MICHIGAN

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DETERMINATION OF THE CHARGE OF POSITIVE THERMIONS FROM MEASUREMENTS OF SHOT EFFECT

BY N. H. WILLIAMS AND W. S. HUXFORD

ABSTRACT

Several new types of current fluctuations have been studied with special reference to the possible effects of both positive ions and electrons, and the influence of space charge. An emitter of positive potassium ions is described which has proven suitable for shot effect measurements. Results indicate that the discharge may be properly controlled and temperature limited currents obtained, giving a value for the K^+ ion equal in magnitude to the electron charge. Values resulting from an extensive series of electron charge determinations confirm the precision and expediency of several new methods which have been introduced into the experimental procedure. A detailed description is given of a simple and direct method of determining the shot circuit impedance.

INTRODUCTION

THE evaporation of electrons from the surface of a hot metal may, under certain conditions, constitute what is known as a *random* process. For this ideal case the statistical distribution-in-time of emission corresponds to the distribution-in-space of the molecules of a perfect gas in equilibrium at a given temperature. If the evaporating electrons are attracted to a positively charged collecting electrode a thermionic current is set up in the evacuated tube. Spontaneous variations of this current may then be expected to conform to the mean square fluctuation law of statistical mechanics. That such fluctuations of the electron stream exist, and that their mean magnitudes may be calculated on the basis of probability theory, was predicted by Schottky,¹ and the phenomenon named by him the "shot effect." He has shown that the magnitude of this effect depends upon the charge, e , carried by a single electron, and has derived an expression for the root mean square value of the potential difference to be expected across a tuned circuit through the coil of which a temperature-limited current is caused to flow.

Various mathematical expressions for the mean square value of the "shot voltage" have been formulated which include circuit constants peculiar to a variety of types of measuring circuits. Those investigators who have used some form of high frequency amplifier in their experiments have obtained results which are uniform and consistent, and which substantiate the essential soundness of the original theory. An outstanding feature of these researches is the unique method provided for the determination of the electron charge. On the basis of the results of these investigations, carried out in circuits having a high natural frequency, the conclusion is reached that, for cathodes composed of metals in the pure state under ideal con-

¹ W. Schottky, Ann. d. Physik 57, 541-567 (1918); W. Schottky, Ann. d. Physik. 68, 157-176 (1922).

ditions, the escape and passage of electrons is a process which is perfectly random in character for currents which are strictly "temperature limited."

INFLUENCE OF SPACE CHARGE

Measurements of the shot effect of a stream of charged particles furnish definite information concerning the probable mechanism of the process of emission and transfer of the particles themselves. Departures from the conditions which give a strictly random distribution may be studied quantitatively with a view to an extension of the theory to account for the observed effects. A striking deviation from the calculated mean square fluctuation has been noted by several investigators when the electron stream is limited by the presence of a negative space charge. There is general agreement that as the space charge is increased the observed current fluctuations become less than theory predicts. In this phenomenon we find the first radical departure from the ideal conditions required for the existence of a random distribution-in-time of the electron passages. When a negative space charge exists between the hot filament and collecting plate the emission and passage of each charged particle does not constitute an event which is independent of every other such event. Electrostatic reactions occur between electrons just being emitted and those existing in the space between electrodes. Experimental results indicate that this condition is one which is under complete control, and that the ideal distribution may be obtained at will by applying a sufficiently high accelerating potential to remove the influence of space charge, or by working with sufficiently small space currents at any stipulated anode potential.

SECULAR CHANGES IN THE EMITTING SURFACE

Violent disagreement exists between results of shot measurements carried out in low frequency circuits and the results obtained with high frequency amplifiers. Investigations at the lower frequencies on both oxide coated and pure tungsten filaments are reported by Johnson.² In general he found the observed fluctuations to be many times larger than was to be expected from the theory, and a decided dependence of the shot voltages upon frequency in the low frequency ranges (e.g., below 200 cycles per second, for a tungsten filament). Johnson concludes "that the large discrepancies between theory and experiment at the lower frequencies are caused by secular changes in the surface conditions of the cathode."

Schottky³ has developed a mathematical theory to account for the phenomena, postulating the presence of foreign atoms in the surface of the emitter which bring about disturbances profoundly affecting the emissivity of the filament during their stay in the surface. The effect may still be thought of as being atomic in nature if the length of stay of the foreign particles in the surface conforms to statistical laws. On the basis of this assumption Schottky derives the frequency distribution of the effect, and by reference to Johnson's measurements calculates the length of stay of

² J. B. Johnson, *Phys. Rev.* **26**, 79 (1925).

³ W. Schottky, *Phys. Rev.* **28**, 103 (1926).

the foreign atom in the surface. For oxide coated filaments this period is estimated to be an average of about 0.001 second, and for tungsten to be greater than 0.05 second. The results of both experiment and theory indicate that the contribution to the total observed fluctuations of these slower secular changes in the emission, as compared to the contributions of the true, or small shot effect, become negligibly small when observations are effected with measuring circuits of high natural frequency.

SHOT EFFECT OF POSITIVE THERMIONS

During the past year a study of the fluctuations which occur in several types of gaseous discharge has been made by the authors. Measurements of the shot effect produced by a "glow" discharge through a gas result, in general, in values of shot voltages ranging from 2.2 to 5 or 6 times that which is to be expected on the basis of Schottky's original theory. The divergence of experimental and theoretical results shows a trend with current density, and there are marked differences in measurements for the same current values in different tubes. The possibility of the production of multiply charged ions fails to furnish adequate explanation of the effects observed.

Any attempt to account for these results must of necessity await a more detailed study of several distinct processes which may be occurring simultaneously in a gaseous discharge. There is the complication due to the presence of both negative and positive charges in the discharge column. It may be expected that the production of ions by collision is a chaotic process; but ionization may be occurring in several well defined regions of the tube, and the enhanced values of shot voltage observed may be due to the superposition of fluctuations arising in these various regions of ionization. In the simple case of thermionic emission of electrons, on the other hand, current fluctuations are due to a random distribution-in-time of charges released only at the surface of one of the electrodes.

Preliminary to further study of discharge streams maintained by the production and passage of both positively and negatively charged particles, it seemed desirable to investigate the shot effect of a space current composed solely of positive ions. In a paper that is largely theoretical, Ballantine⁴ mentions having worked with caesium ions; with this exception, the writers are not aware of any attempts to determine the charge of a positive ion by measurements of shot effect. A suitable current composed of positive charges is more difficult to obtain than a current of electrons, and the conditions for perfectly random fluctuations may be expected to be harder to realize because of the large mass of the carrier. In the following paragraphs a positive ion source is described which seems to fulfill the desired conditions and it has been found possible to secure the ideal distribution-in-time of emission which must be realized in order to apply probability theory to the process. A detailed study of the influence of space charge has been made in an attempt to secure sufficient data upon which to build a mathematical theory of this effect.

⁴ Stuart Ballantine, *Jour. Franklin Inst.* 206, 159 (1928).

SOURCE OF POSITIVE IONS

Two types of sources of positive ions were considered. First, a special type of gas tube in which the ion stream is produced by collisions of gas molecules and electrons emitted by a hot filament. This kind of source is highly desirable for a study of fluctuations arising during the process of ionization. It is hoped that a tube operating upon this principle and suitable for shot measurements may be evolved in the near future.

The second type to be considered was a highly evacuated tube containing an emitter of positive thermions. Such a tube seemed preferable for first tests on positive ions, but certain limitations seemed at first to preclude its use for shot measurements. Several forms of heated anodes were tested in an effort to obtain a steady emission of ions, and at the same time to secure currents large enough to produce measurable shot voltages. Considerable experimentation revealed a method of constructing an emitting element which produces an ion stream of convenient magnitude, and which is sufficiently stable for carrying out accurate measurements. This type of source was first described by Kunsman,⁵ and consists of a fused mixture of iron oxide and about one percent of an oxide of an alkali or alkaline earth metal. Various samples of a potassium-iron oxide mixture were made and tested, and the emission was found to be quite steady at temperatures up to about 850°C.

The mixture finally used in the construction of the shot tube was one of potassium and iron oxides kindly furnished by the Fixed Nitrogen Research Laboratory through the courtesy of Dr. C. H. Kunsman. The fused oxide mixture was ground to a fine powder of 300 mesh and smaller and placed in alundum boats in the electric furnace. Here the powder was reduced in an atmosphere of hydrogen for twenty-six hours, at a temperature of 920°C. The reduced metallic mixture was pulverized a second time and a thin paste formed by mixing it with paraffin oil. This paste was used in forming the active element, or anode, of the emission tube.

The anode consists of a coil of fifty turns of 20 mil tungsten wire, previously cleaned and roughened with sand paper, wound on a hollow quartz tube approximately 8 mm in diameter and 6 cm long. The terminals were spot welded to iron lugs and these clamped to 125 mil tungsten electrodes fused through the ground glass stopper. In the second form of tube no ground stopper was used, the tube being directly connected to a vacuum system. The oxide paste was spread on the coil of wire, previous to mounting, by means of a small brush. Preliminary tests showed that it was of advantage to coat also the quartz tubing between the turns of wire. After each coating had been applied the coil was heated in air by passing a current through it and a temperature reached at which the mixture glowed to a bright red as fusion took place. This fusion bound the mass firmly to the coil. Successive coatings were applied and each heated in the same manner until depressions between turns were filled. When a current is passed through the wire the

⁵ C. H. Kunsman, *Science* **62**, 269 (1925).

heat spreads evenly throughout the cylindrical shell of oxides, and upon cooling none of the mass falls off or becomes loosened.

A charcoal chamber was connected directly to the first tube used, and was immersed in liquid air while measurements were being made. This effectively absorbed any gas given off from the oxides during emission, as well as gas from the cement used in sealing the ground joint. Other investigators working with this type of emitter have found it desirable to carry out a second reduction of the materials, oxidation having taken place in the process of fusing the metals in air. This was found to be unnecessary in the present work, however, no hydrogen being admitted to the tube after the coil was mounted.

The cathode consists of a cylinder of nickel about 12 mm in diameter, mounted coaxially with the quartz tube. The mean clearance between oxide coating and inner surface of the cathode is about 1 mm, which provides a means of obtaining a high potential gradient between emitting element and collecting plate. For the earlier trials, the tube used had an outer cylinder 7 cm in length; when later the electrodes were mounted in a system in which all seals were of glass, it became necessary to shorten the cylinder to 5 cm, which was about the length of the active emitting element. Before shot measurements were taken the metal parts of the tube were thoroughly baked out by means of the induction furnace until the gas pressure was reduced to 10^{-6} mm of mercury or lower.

A total emission of 1200 microamperes was attained at a temperature of about 900°C , but this fell off rather rapidly with time. Currents in the neighborhood of 400 microamperes were quite steady in character, falling off less than 5 percent in one hour of constant operation of the tube. When placed in the shot circuit the discharge of positive ions gave constant values of shot voltage for each value of emission current, and the results could be checked within the limits of error of the measuring circuit. For values in the neighborhood of 1200 microamperes positive ion current, a reversal of the accelerating potential indicated an electron current of approximately 12 microamperes. For lower positive emission, at lower temperatures, the ratio of electron current to positive ion current was even less; the reverse was true if the temperature of the emitter was raised.

THE APERIODIC SHOT CIRCUIT

The type of shot circuit used in the measurement of the positive ionic charge is shown in Fig. 1. f is the hot electrode of an evacuated tube, p the collecting plate connected to the negative terminal of the battery through a resistance R . C represents the capacitance to ground of the plate and connecting wires. The hot electrode is connected through large condensers to the grounded copper box and hence there are no high frequency variations of its potential. The fluctuations of the space current due to random thermionic emission cause variations of the potential of the plate which is connected to ground only through a conductor of large impedance. When this electrode is joined to the grid of the first tube of an amplifying

system, these variations in potential furnish a voltage input to the system. This voltage is amplified and finally detected and measured on an output galvanometer. The deflections of this galvanometer are proportional to the mean square values of the input potentials.

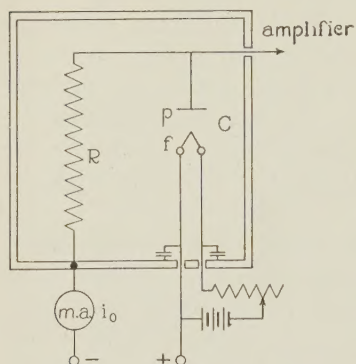


Fig. 1. Aperiodic shot circuit.

This type of circuit is the familiar aperiodic shot circuit described by Williams and Vincent.⁶ It has been shown by them that the total mean square output voltage, $\bar{E}^2$, of the amplifying system is given by the equation,

$$\bar{E}^2 = 2Z^2 A_0^2 i_0 \epsilon A, \quad (1)$$

where Z is the impedance of the shot circuit, measured at the resonance frequency of the amplifier; A_0 the voltage amplification at the same frequency; i_0 the total emission current in the shot tube; ϵ the value of the charge

carried by each particle emitted from the hot electrode; and A the area under the curve which represents relative voltage amplification plotted against frequency.

If the shot circuit be disconnected from the amplifying system and a known potential, v_i , be applied to the input, then when this potential has a frequency equal to that of the resonance frequency of the amplifier, it becomes after amplification equal to $A_0 v_i$. If v_i is adjusted so that it produces the same output as the shot voltage, we then have

$$\bar{E}^2 = A_0^2 v_i^2 = 2Z^2 A_0^2 i_0 \epsilon A,$$

from which

$$\epsilon = \frac{v_i^2}{2Z^2 i_0 A}. \quad (2)$$

From this equation the electronic or thermionic charge may be determined by the measurement of a high frequency voltage, the impedance of the shot circuit, a direct current reading, and a factor which is characteristic of the amplifying system

THE AMPLIFIER

The measurement of high frequency voltages ranging from two to ten microvolts is an essential part of this investigation. For this purpose an amplifier similar to that used by Hull and Williams in their first measurement of the electron charge was employed. It is a five stage amplifier with tuned impedance coupling and makes use of the shielded grid pliotrons which were developed at the Research Laboratory of the General Electric Company and described by Hull and Williams⁷ in 1926. Each stage of the

⁶ N. H. Williams and H. B. Vincent, *Phys. Rev.* **28**, 1250 (1926).

⁷ A. W. Hull and N. H. Williams, *Phys. Rev.* **27**, 432 (1926).

amplifier is in a separate metallic box. The connection to the control grid of each tube is through its upper end and this end of the tube projects through a hole in the floor of the compartment above. The elaborate shielding is necessary to prevent regeneration and self-oscillation. The plate coil of the final stage is coupled to a coil supplying current to a thermocouple. The wires leading from this couple to the galvanometer outside the box are provided with filters to prevent high frequency currents from getting outside the amplifier box. The entire apparatus is enclosed in a large wire cage.

The grid biases on the amplifier tubes must be so adjusted that the output current read by the galvanometer is accurately proportional to the mean square of the input voltage. The resonance curve covered a range from 112 to 121 kilocycles, and when the amplifier was carefully tuned it was found to be very nearly symmetrical.

The voltage factor, v_i , of Eq. (2) represents the potential of known value, having a frequency equal to that of the amplifier circuits, which when applied to the amplifier will produce the same output current as that produced by the shot voltage. The method used to determine v_i is one of substitution, and it is essential that the regeneration when the shot circuit is connected to the grid of the first tube shall not be different from that when the calibrating voltage is applied. In order to test this, a high frequency voltage is applied to the grid of the second tube of the amplifier, this voltage having a proper magnitude to give a deflection of the output galvanometer as large as that normally obtained. The connection to the grid of the first tube is then shifted from the shot circuit to ground and back to shot circuit. In every test made this has resulted in producing not the slightest change in the deflection of the output galvanometer. From this it appears that, when the input grid circuit has a high resistance and little inductance as in this case, it is entirely safe to use a substitution method in measuring the input voltage.

THE CALIBRATING VOLTAGE

An inductance potentiometer of the type used by Hull and Williams⁸ furnishes the calibrating voltage, v_i . This apparatus is shown in Fig. 2.

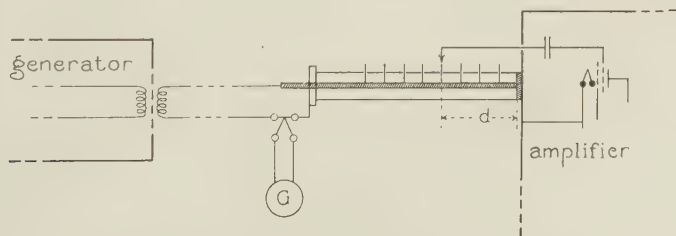


Fig. 2. Inductance potentiometer.

A high frequency current flows in along the quarter inch rod and returns along the coaxial cylinder. An attenuator is used so that the current actually

⁸ A. W. Hull and N. H. Williams, Phys. Rev. **25**, 147 (1925).

measured is considerably larger than that used in the inductor. The calibrating voltage is the inductive drop over a short length of the rod. The rod in the device used by Hull and Williams was of copper and the frequency was greater than 700 kilocycles per second. Under such conditions the penetration of the current into the rod is slight and the inductance per unit length is given quite accurately by the expression, $L = 2 \log_e(R/r)$, R being the inner radius of the shell and r the radius of the rod. Because of the lower frequency used in this work and also because the rod was of brass instead of copper, it is necessary to correct this formula for the effect of penetration, i.e., it cannot be assumed that the current is confined to a layer of the metal very near the surface. A. Russell⁹ has derived an expression for the inductance of such a coaxial main in terms of the two radii, the resistivity of the metal and the frequency of the oscillation. Making use of Russell's formula, the inductance per unit length of the potentiometer is computed, and the calibrating voltage, v_i , is given by the expression $Ld\omega_0 i$ (in which d is the length of rod used, $\omega_0/2\pi$ the resonance frequency of the amplifier, and i the current), since the resistance is insignificant and the wave is harmonic. The authors believe that this method of measuring high frequency voltages of the order of five microvolts is subject to an error of less than one percent.

THERMOJUNCTIONS

It is frequently impossible to obtain accurate values of high frequency current by means of thermojunctions when the entire heating element is employed. This becomes evident when one considers the fact that capacity currents occur through the galvanometer which is used to indicate the direct current generated by the junction. Thus the high frequency current through one-half the heating wire may in certain cases be several times as great as that through the other half. This difficulty is obviated by using but one-half of the heater, in which case one of the high frequency connections is made at the same place as one of the galvanometer leads.

This restriction to the use of "half" junctions requires that calibrations be carried out with low frequency alternating current. Values of a.c. potentials may be determined by comparison with the e.m.f. of a standard cell, using a circuit in which there is an auxiliary thermojunction in series with a resistance. A "standard" deflection is found, corresponding to a known voltage, by means of a balance obtained with direct current. This deflection is duplicated when alternating current is applied, the value of the alternating current flowing through the half-junction to be calibrated being calculated in terms of the standard cell e.m.f. and values of standard resistances. All such calibrations are carried out with the half-junction and its galvanometer in the position in which they are to be used for shot measurements. Frequent repetition of this calibration is necessary to eliminate errors due to deterioration of the heating elements with use.

⁹ A. Russell, *Phil. Mag.* **17**, 524 (1909).

IMPEDANCE OF THE SHOT CIRCUIT

The impedance factor Z , of Eq. (2) is the only circuit constant required for the evaluation of the electronic or ionic charge. A method of determining its value has been devised which, for simplicity and ease of computation, is comparable with the operations necessary in the measurement of the voltage factor, v_i . The circuit arrangement used is shown in Fig. 3.

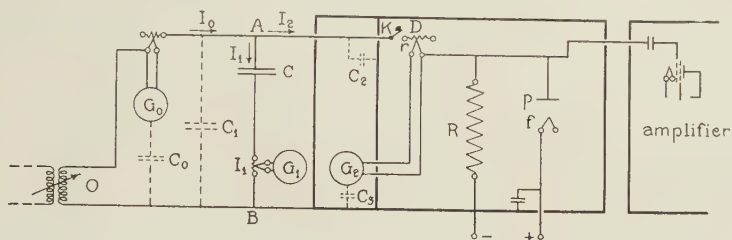


Fig. 3. Measurement of impedance.

A special study was made of various kinds of resistors suitable for use in the aperiodic shot circuit. It was found that graphite resistors were not constant over long periods of time and frequently were subject to rapid and erratic variations. A very convenient form of wire resistance coil consists of fine chromel wire wound in shallow grooves on a bakelite cylinder about 9 cm in diameter. One such coil of 150 turns had a resistance of 34,030 ohms. Ordinary commercial types of radio grid leaks exhibit an erratic current fluctuation which becomes more pronounced with ageing. A particular brand of vacuum grid leak has been tested and found to produce no observable shot fluctuations. This type of resistor has the advantage of extreme compactness, and its use reduces the total electrostatic capacity of the shot circuit. Both chromel wire resistors and vacuum grid leaks were used in making measurements, and were found to be satisfactory in every respect.

In Fig. 3 R represents such a resistor; it forms the connection from the plate of the shot tube to a grounded point on the copper shield. The other electrode of the tube is shunted to ground through a 1 microfarad condenser, thus effectively confining the high frequency currents to that part of the circuit contained within the shielding box. The electrode p is joined by means of a grid condenser to the grid of the first tube of the amplifier, and also to one terminal of a half-junction arrangement which is used to measure the input current for impedance calibration. While the circuit is operating under precisely the same conditions as those used in the determination of shot voltages, measurements of impedance are carried out in the manner described below.

A coil O , which with its leads is enclosed in an electrostatic shield, is coupled electromagnetically with a coil in the tuned plate circuit of a dynatron oscillator having the same frequency as that of the amplifier. This coupling is variable, and completely controlled by the operator from within the large wire cage. The coil is connected through a vacuum junction to the terminals A, B , of a standard condenser. Current I_1 passing through this condenser heats the entire element of a low resistance thermocouple, pro-

ducing deflections on the galvanometer G_1 . The capacity current from G_1 to ground, which flows through but one-half the heater of the couple, is in quadrature with the current through the other half which has a resistance of only 17 ohms. It is wholly negligible by comparison with the total current.

When the current I_1 is known, the potential across A, B is given by

$$V' = I_1 / C\omega_0,$$

where C is the capacitance of the standard condenser. The small potential drop across the resistance of the junction is in quadrature with V' and may be neglected.

The entire impedance of the circuit within the shielding compartments is now given by

$$Z' = V' / I_2 = \frac{I_1}{I_2} \cdot \frac{1}{C\omega_0}. \quad (3)$$

It is to be noted, however, that this is not precisely the impedance of the shot circuit as it is used in conjunction with the amplifier in the calculation of shot voltages. The impedance required is the impedance Z of that part of the circuit included between the point D , and the ground point B . A correction must be applied for the series resistance r of the half-junction through which I_2 flows.

Let v represent the root mean square value of the potential drop across r ; it is equal in magnitude to $I_2 r$, where r has the same value of resistance for direct current as for high frequency current, being a short piece of very fine wire. If V is the root mean square value of the potential across DB , then we have the vector relation,

$$\vec{V'} = \vec{V} + \vec{v} \quad (4)$$

We may calculate the potential V by determining the phase angle, ϕ , between v and V' , and then the correct impedance of the shot circuit is given by $Z = V / I_2$.

Let I_0 represent the total input current from the generator as read by G_0 when the switch K is closed, I_1 the current through C and I_2 the input to the shot circuit. If the switch K is now opened, the coupling of O may be adjusted until G_1 indicates the same value of I_1 as before. The current through the input junction as registered by G_0 will now be different; let its new value be represented by I_1' . This current is wholly a capacity current, and is the current through C plus all currents through such line capacities as are represented by C_1 and c_2 . Since the potential from A to B is now the same as in the first operation with K closed, I_1' represents all capacity currents external to the shot circuit which were

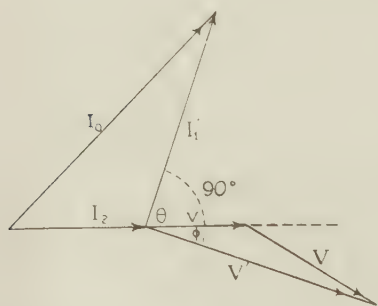


Fig. 4.

flowing in the first case. We have then for the currents with K closed the vector equation,

$$\vec{I}_0 = \vec{I}_1' + \vec{I}_2.$$

If θ designates the phase angle between I_2 and I_1' we have (Fig. 4),

$$I_0^2 = I_1'^2 + I_2^2 + 2I_1'I_2 \cos \theta,$$

from which

$$\cos \theta = \frac{I_0^2 - (I_1'^2 + I_2^2)}{2I_1'I_2}. \quad (5)$$

Since I_1' is 90° out of phase with the potential V' across the standard condenser, the phase angle ϕ , between v (in phase with I_2) and V' , is given by $\phi = 90^\circ - \theta$, and $\cos \phi = \sin \theta$. Eq. (4) for the potentials may now be rewritten as follows,

$$I_2^2 Z^2 = I_2^2 Z'^2 + I_2^2 r^2 - 2 \sin \theta I_2 r \cdot I_2 Z'.$$

Cancelling the common factor I_2^2 , and taking the square root of both members of this equation, the impedance is given by the equation

$$Z = Z' \left(1 - \frac{2r \sin \theta}{Z'} + \frac{r^2}{Z'^2} \right)^{1/2}. \quad (6)$$

This is the value of Z required by Eq. (2). It is expressed in terms of a directly measureable quantity

$$Z' = \frac{I_1}{I_2} \cdot \frac{1}{C\omega_0},$$

multiplied by a correction factor depending upon Z' , r (460 ohms in the present experiments), and an angle, θ , calculated from Eq. (5). For the case of high impedances ($Z > 20,000$ ohms) for which large values of R must be used, $\sin \theta \doteq 0$, and $Z = Z'$. For very low impedances, in which R is small and of the order 10 r , $\sin \theta \doteq 1$, and $Z = Z' - r$.

The greatest uncertainty in the value of Z computed from Eq. (6) is that introduced in the value of the capacitance, C . For this work C is obtained by means of a standard condenser, mounted in a copper box and calibrated at the U. S. Bureau of Standards. The probable error is 2 parts in 1000.

FREQUENCY STANDARDIZATION

Values of frequency used in these measurements were initially obtained by means of a wave meter having a Bureau of Standards calibration, and were subject to an error of 0.3 percent. Near the termination of the work, however, absolute frequency standardization of a quartz crystal was carried out in the laboratory by Mr. Donald Lowe. The method used provided a means of tuning harmonics of the input to the amplifier to a harmonic of the crystal, and obtaining accurate condenser settings on the amplifier by the

TABLE I. *High space currents.*

	i_0 Microamperes	Z Ohms	v_1 Microvolts	ϵ Coulombs $\times 10^{-19}$
$A = 3500$	1988	16,540	24.73	1.607
$n_0 = 116,800$	2196	16,530	26.07	1.618
$R = 40,100$	2970	16,386	30.00	1.612
	2970	16,478	30.00	1.594
	1978	16,620	24.93	1.625
	2970	16,478	30.18	1.613
	1978	16,620	24.58	1.580
	2970	16,478	29.76	1.568
			Mean	1.602
$A = 3500$	1978	16,390	24.26	1.582
$n_0 = 116,800$	2970	16,070	29.41	1.611
$R = 40,100$	1978	16,390	24.29	1.586
	2970	16,070	29.30	1.599
			Mean	1.595
$A = 3511$	2970	16,671	30.32	1.586
$n_0 = 117,000$	2970	16,671	30.13	1.566
$R = 34,030$	2970	16,671	30.11	1.564
	1978	16,878	24.93	1.570
	1978	16,878	24.95	1.573
	1978	16,878	25.23	1.608
			Mean	1.578
$A = 3511$	2030	17,110	25.69	1.581
$n_0 = 117,400$	2030	17,110	25.87	1.604
$R = 34,030$	2030	17,110	25.90	1.608
	2978	16,960	30.55	1.551
	2978	19,960	30.88	1.585
	2978	19,960	31.04	1.602
			Mean	1.589*
$A = 3511$	2030	17,110	25.69	1.581
$n_0 = 117,400$	2030	17,110	25.80	1.595
$R = 34,030$	2030	17,110	25.86	1.603
	2978	16,960	30.78	1.575
	2978	16,960	30.75	1.572
	2978	16,960	30.94	1.592
			Mean	1.586*
$A = 3511$	4553	13,990	31.60	1.596
$n_0 = 117,400$	4553	13,990	31.42	1.578
$R = 21,500$	4553	13,990	31.74	1.610
	3530	14,130	27.99	1.583
	3530	14,130	27.97	1.581
	3530	14,130	28.12	1.598
	2496	14,190	23.66	1.586
	2496	14,190	29.91	1.600
	2496	14,190	23.78	1.602
			Mean	1.593*

* These measurements were taken under the most favorable conditions, and the results are given double weight in the final average.

method of beats. The fundamental reference frequency was a 60 cycle current from a tuning fork, which operated a motor driven clock. The clock was

rated against Arlington time signals, and the estimated error of this operation is ± 0.5 sec. in a period of ten hours.

When the wave meter indicated a frequency of 117.0 kilocycles, tests by the beat method against crystal gave 117.1 kilocycles. This indicates that the frequencies throughout the series of shot measurements are subject to a probable error of 0.1 percent.

PRELIMINARY ELECTRON CHARGE MEASUREMENTS

An extended series of measurements of the electron charge was undertaken with two objects in mind: to test the efficacy and precision of the new method of impedance measurement, and to study the effect of wide variations in magnitude of the electron emission. Tables I and II give the results obtained with two highly evacuated tubes having straight wire

TABLE II. *Low space currents.*

	i_0 Microamperes	Z Ohms	v_1 Microvolts	Coulombs $\times 10^{-19}$
$A = 3511$	194.4	19,700	9.181	1.591
$n_0 = 117,000$	174.6	19,700	8.699	1.590
$R = 50,000$	155.4	19,700	8.203	1.592
	136.0	19,700	7.634	1.572
	115.8	19,700	7.006	1.555
	97.4	19,700	6.410	1.548
	77.2	19,700	5.742	1.567
	58.3	19,700	4.986	1.565
	39.5	19,700	4.200	1.639
	20.5	19,700	3.020	1.632
			Mean	1.585
Final average (weighted)				$1.589 \cdot 10^{-19}$ coulomb
Millikan's value for $e =$				$1.591 \cdot 10^{-19}$ "

tungsten filaments and cylindrical plates. A plate potential of 100 volts or more insured that the currents were "temperature limited." Stable conditions in the amplifier circuits were secured by a preliminary heating of the tube filaments for a period of from thirty to forty minutes. Tests before and after a set of observations of shot voltages showed a variation of less than 0.2 percent, in the value of the amplification factor A which was obtained by direct measurement of the area under the plotted resonance curve. Each value of e given in the tables represents the mean of several separate determinations of impedance and of equivalent shot voltage, v_1 . R is the direct current value of the resistance used in the circuit, n_0 the frequency in cycles per second, and i_0 the electron space current.

MEASUREMENT OF THE CHARGE OF K^+ THERMIONS

The simplicity and precision of this method of measuring shot effect render it particularly suitable for the investigation of newly discovered fluctuation phenomena which, in certain cases, require a large number of observations and rather elaborate apparatus for control of the discharge.

This has proven to be true in the study of the thermionic emission of positive ions. The greater part of the labor involved in this work has been the devising of schemes to obtain a properly controlled emission. The tube used in the shot circuit must be kept on the evacuating system, and all measurements reported were carried out with a gas pressure in the tube not greater than 10^{-5} mm of mercury. Potentials up to 1000 volts were furnished by batteries located inside the operator's cage, and the positive ion emitter required a special system of filament control. Observations were checked by many repetitions of shot voltage and impedance measurements for each condition in the shot circuit.

The following table shows the summary of shot measurements as first taken with the tube emitting potassium ions. An attempt was made to eliminate as far as possible the influence of space charge, cathode potentials being increased for the larger ion currents. Results for the observed value of ϵ , the ionic charge, indicate that the space charge was probably only partially removed.

TABLE III. *Charge of the potassium thermion.*

Cathode potential	Space current (microamperes)	v_1 (microvolts)	Impedance Z (ohms)	ϵ (coulombs $\times 10^{19}$)
180 volts	20.4	2.926	19,510	1.597
180 volts	39.8	4.087	19,480	1.602
180	59.0	4.962	19,440	1.599
180	77.8	5.639	19,430	1.570
226	97.8	6.345	19,400	1.584
226	117.0	6.930	19,380	1.583
226	155.1	7.366	19,360	1.552
226	154.1	7.833	19,340	1.542
316	174.6	8.336	19,320	1.545
316	194.8	8.788	19,300	1.542

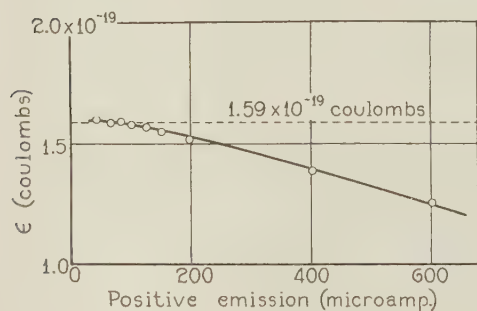


Fig. 5. Apparent values of the charge of potassium ions obtained with a constant plate potential of -270 volts. The limiting value of ϵ for low current densities is approximately 1.596×10^{-19} coulomb.

approaches zero is approximately equal to $1.596 \cdot 10^{-19}$ coulomb.

A second series of measurements was undertaken in which a constant tube potential was maintained, and the limiting value of ϵ for low current densities determined. This limiting value then constitutes a close approximation to the true value of the positive ionic charge, since with small current densities the condition for temperature-limited currents, as required by theory in the derivation of the shot equation, is realized. The results are shown graphically in Fig. 5, and the limiting value approached by ϵ as i_0

A further study of the influence of space charge was carried out by maintaining a constant ion current through the tube and varying the cathode potential. The results are shown in the plot of Fig. 6. Each point represents a separate determination of ϵ , the apparent charge, as calculated from Eq. (2), impedance measurements being taken in each case at the potential used for equivalent shot voltage calibration. The dotted curve *A* represents the result obtained while using the first tube in which the cylindrical plate was 7 cm in length, the constant space current 400 microamperes. For the second mounting of the emitting element the cylindrical cathode was shortened to 5 cm and the comparative effectiveness of the two cylinders in removing space charge is clearly indicated. Curve *B* shows the results with the second mounting, space current 200 microamperes; curve *C*, with space current equal to 400 microamperes.

A recent investigation of oxide emitting elements reveals many interesting features with regard to fluctuations arising in discharge streams in which both positive ions and electrons occur simultaneously. Results of these studies, to be published shortly, give a possible explanation of the sharp downward bend in the curves of Fig. 6. For cathode potentials below 100 volts the temperature of the emitting anode was increased to such a degree that the cathode, viewed inside the closed copper box, showed a dull red glow. Probably some electron emission from the cylinder occurred under these conditions and accounts for the rather sudden decrease in the apparent value of ϵ . For the longer and flatter part of the curves, the slopes are found to be roughly proportional to the inverse square roots of the masses of the ions when compared to similar curves for barium ion emission in a tube having electrodes of the same dimensions, when the emission current was of the same magnitude.

There is one particular in which all tests are in agreement. Under the condition of a sufficiently large accelerating potential (or, for a given potential, a sufficiently small current), the limiting value of ϵ is $1.59 \pm 0.01 \cdot 10^{-19}$ coulomb, and in not a single case has this value been exceeded by an amount in excess of the estimated error of observation. The conclusion to be drawn from the results of some fifty observations of the current fluctuations arising in discharge streams maintained by the thermionic emission of potassium ions, is that the method of measuring the ionic charge by the shot effect is entirely feasible in properly constructed emitting tubes. These studies

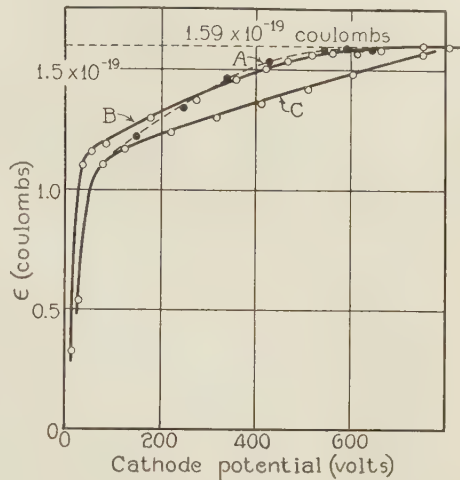


Fig. 6. Apparent values of the charge of the K^+ ion obtained by holding the emission current constant and changing the cathode potential.

introduce a new and interesting method of observing the influence of space charge under conditions not usually realized in other forms of experimental procedure. A further study of the shot effect of various elements used in conjunction with the iron oxide catalyst should furnish independent contributory determinations of ionic charges to those already obtained by mass spectrograph measurements.¹⁰

POSITIVE ION EMISSION

The results here presented indicate that whatever may be the mechanism by which the oxide crystals effect the release of the potassium ion, it is such that the distribution in time of the emission is a perfectly random one. No doubt the factor which determines the distribution is the probability of the acquiring by the atom of sufficient energy to separate it from its single valence electron when the atom is near the surface of the hot anode. Kunsman's¹¹ results on the value of the work function of vaporization of positive ions indicate that atoms of the alkali and alkaline earth metals escape as positive ions, rather than as neutral atoms, because the value of the function ϕ , or the work required to remove an electron from the oxide mixture, is greater for an outer, or conduction, electron of the atom than the work required to separate the electron from the atom. Thus the probability that an electron will escape from the surface is very much less than that a positive ion will escape. Emission tests at temperatures below 900°C, carried out in conjunction with the present work, indicate that, in no case, was the electron emission greater than one percent of the positive ion emission.

DEPARTMENT OF PHYSICS,
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¹⁰ Barton, Harnwell and Kunsman, *Phys. Rev.* **27**, 739 (1926); and others.

¹¹ C. H. Kunsman, *Jour. Phys. Chem.* **30**, 525 (1926); *Jour. Franklin Inst.* **203**, 635 (1927).

